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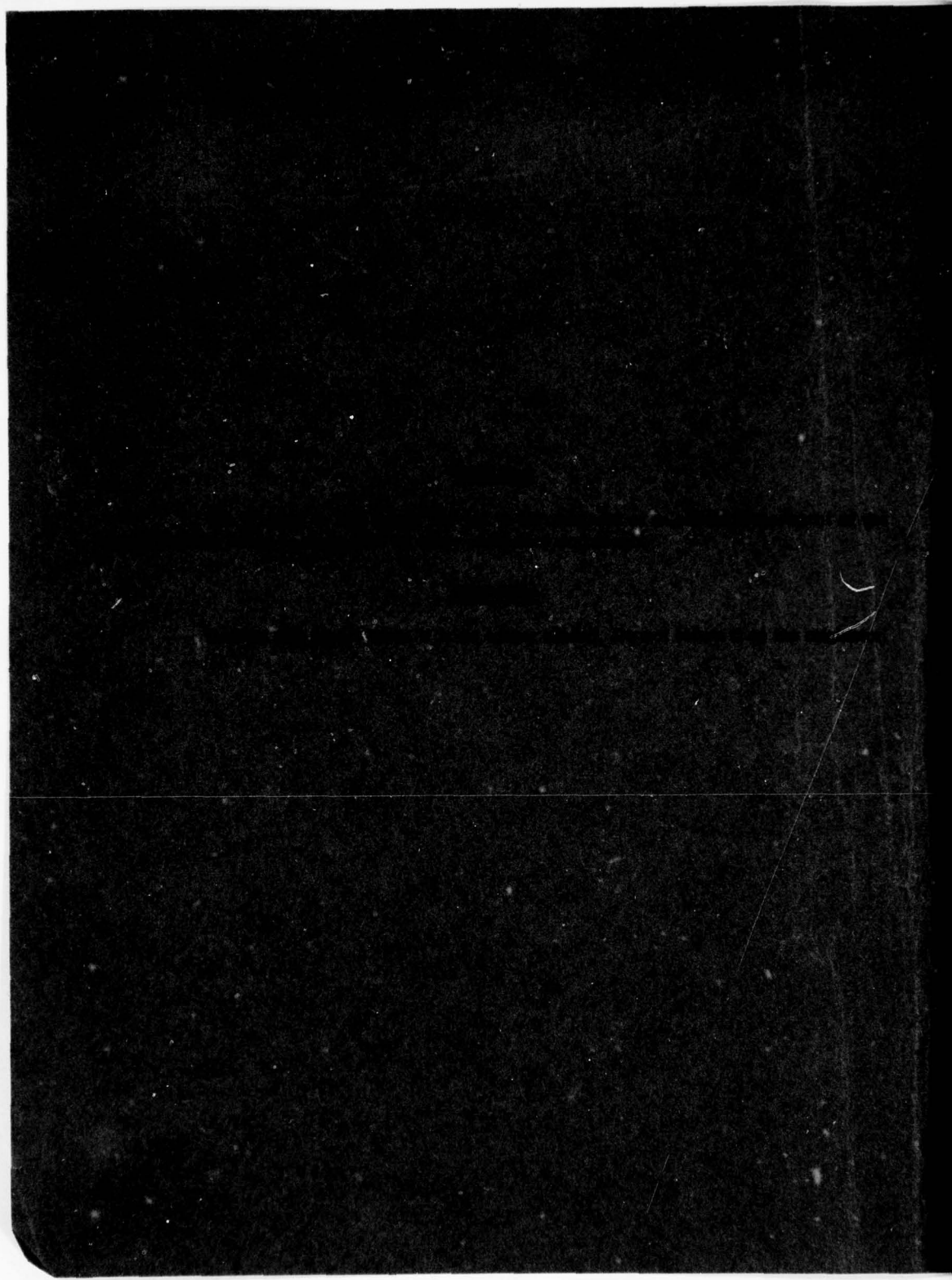
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (U) This report is intended as a guide for electro-optical applications engineers interested in the effects of polymolecular clusters of water upon infrared transmission of the atmosphere. It is a compendium of work on the subject ranging from the oldest to the newest, some of which is not yet generally accepted by the scientific community. A theoretical model for infrared absorption spectra due to intermolecular hydrogen bonding is developed from a simple cluster model. Expressions leading to approximate values of hydrogen-bond strength are developed, allowing (Continued on reverse side)		

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20. ABSTRACT (Contd)

equations and curves to be derived, from data in the literature, for equilibrium cluster concentrations in moist air or water vapor, as functions of saturation ratio and temperature. The very large differences in absorptivity between water in the vapor and liquid phases are explained, as are "pressure-squared" and inverse temperature dependencies of water cluster absorption in the infrared. Applications are suggested.



PREFACE

The work described in this report was authorized under In-House Laboratory Independent Research (ILIR). This work was started in January 1977 and completed in December 1977. The experimental data are recorded in notebook 9613.

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INTRODUCTION TO POLYMOLECULAR WATER CLUSTERS AND THEIR INFRARED ACTIVITY

I. INTRODUCTION.

Water vapor is one of the key atmospheric constituents whose absorption spectra or rather the wavelength regions of relatively high transmission between absorption bands define the infrared "window" regions in which most infrared instrumentation must operate. Two important window regions, extending from 3 to 5 μm and 8 to 13 μm , are utilized by a wide variety of infrared instrumentation designed to look through intervening atmosphere at remotely-located targets. Such instruments can function to image the targets, to measure radiometric characteristics of them, or for a variety of applications. Until recently, it was assumed that atmospheric water was found in one of three phases: vapor (monomer), liquid droplets, or ice crystals. Now it is believed by some workers, including the author, that a polymolecular cluster phase of water exists in the vapor phase, also. These clusters are believed to consist of many water molecules gathered about small ionic nuclei, always present in "real" atmospheres and in the cleanest of laboratory apparatus. Too small to attain "critical" size and thus to become liquid water droplets, they nevertheless should influence infrared absorption and emission by vapor samples very significantly.

II. WATER VAPOR.

The infrared transmission spectrum of water "vapor" is shown in figure 1. The vapor spectrum is dominated by absorption bands attributed to interatomic vibrations of the hydrogen and oxygen atoms comprising the water molecules. For example, the band at 2.76 μm is due to H-O stretching, whereas the band at 6.27 μm (which has "bottomed out" in figure 1) is due to more complex vibrational modes of the water molecule which are also interatomic modes. Beyond 13 μm , water vapor has increasing absorption which rises to a broad peak near 50 μm . This latter peak is attributed to rotational modes involving entire water molecules but it may also involve clusters of water molecules as will be discussed presently.

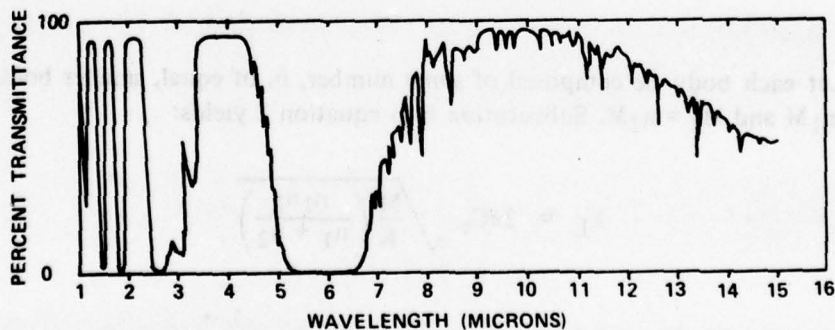


Figure 1. Infrared Transmittance of Water Vapor

III. A SIMPLE WATER CLUSTER MODEL.

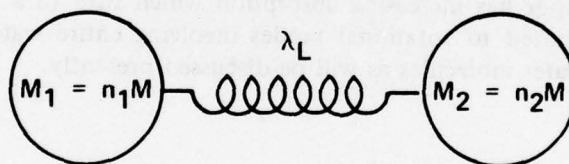
If, instead of single water "vapor" molecules, we now consider clusters of water molecules held together by hydrogen bonding, the intermolecular hydrogen bonds also would be expected to have infrared absorption bands at wavelengths corresponding to frequencies of their vibrational modes. The simplest possible vibrational mode involving a given hydrogen bond would be linear stretching. This mode would be associated with the highest-frequency (shortest-wavelength) absorption bands of water clusters. Although progressively more complex cluster vibrational modes would account for absorption at longer wavelengths, it should be possible as a first approximation to consider the simplest case using the classical expression for a two-body oscillator:

$$\lambda_{\mu m} = 2\pi C_v / \sqrt{K \left(\frac{1}{M_1} + \frac{1}{M_2} \right)} \quad (1)$$

where C_v is the velocity of light, M_1 and M_2 are the masses of the two bodies, and K is a constant. Equation 1 can be rewritten in the form:

$$\lambda_{\mu m} = 2\pi C_v \sqrt{\frac{1}{K} \left(\frac{M_1 M_2}{M_1 + M_2} \right)} \quad (2)$$

Now consider the perfectly general case of equations 1 and 2 for an oscillator consisting of two bodies vibrating about a single "spring" or bond, so that the vibrations occur at a wavelength λ_L :



Let each body be composed of some number, n , of equal, smaller bodies of mass M , so that $M_1 = n_1 M$ and $M_2 = n_2 M$. Substitution into equation 2 yields:

$$\lambda_L = 2\pi C_v \sqrt{\frac{M}{K} \left(\frac{n_1 n_2}{n_1 + n_2} \right)} \quad (3)$$

where K must be empirically evaluated.

For example, if the oscillator consisted of water molecules, hydrogen-bonded together to form a polymolecular cluster, then M would equal 18 and $n_1 + n_2$ would sum to the number of water molecules in this particular cluster, which we shall call " c ." Furthermore, the absorption band wavelength, λ_L , would be independent of the actual configuration of molecules on either side of this particular intermolecular bond. They could be in branched or straight chains or in "favored" geometric shapes such as tetrahedrons. For this simple analysis, however, consider a cluster of 13 water molecules hydrogen-bonded together into a straight chain.

There are $(c-1)$, or 12, hydrogen bonds in this cluster, which will be assumed for simplicity's sake to be of equal strength. These bonds are arranged in six "pairs," each equidistant from the center molecule of the chain. Hence, from equation 3, there will be six characteristic absorption wavelengths for this cluster, corresponding to the following combinations of chain lengths:

No. of bonds	n_1	n_2	$\sqrt{\frac{n_1 n_2}{n_1 + n_2}} = \sqrt{\frac{n_1 n_2}{c}}$
2	6	7	1.80
2	5	8	1.75
2	4	9	1.66
2	3	10	1.52
2	2	11	1.30
2	1	12	0.96

Since all other terms are constants in equation 3, the absorption spectrum of this cluster should consist of the envelope of absorption bands which are wavelength-distributed according to the expression $\sqrt{n_1 n_2 / c}$. As can be seen in figure 2, this spectrum arising from intermolecular bonds should increase in absorption with increasing wavelength, assuming equal hydrogen-bond strength throughout the cluster. If the bond strength does become weaker toward the ends of the cluster, the slope of the spectrum in figure 2 will become even greater since the position of the strongest absorption bands will correspond to near-symmetrical values of n_1 and n_2 from equation 3.

The form of equation 3 insures that the most-symmetrical cluster hydrogen-bond configurations correspond to closest-packed absorption bands and, thus, to a peak absorption by the cluster at a wavelength which we can call λ_{\max} . For less-symmetrical configurations, the absorption wavelength is always shifted toward smaller values. For this reason, the cluster absorption spectrum will always increase with wavelength toward λ_{\max} , where it will peak and fall rapidly beyond this wavelength. Therefore, $n_1 = n_2$ is a special case which determines λ_{\max} . Since $c = n_1 + n_2$, for this special case $n_1 = n_2 = c/2$; that is, we would expect to find λ_{\max} for a typical water cluster at a wavelength proportional to $\sqrt{c/2}$, from equation 3.

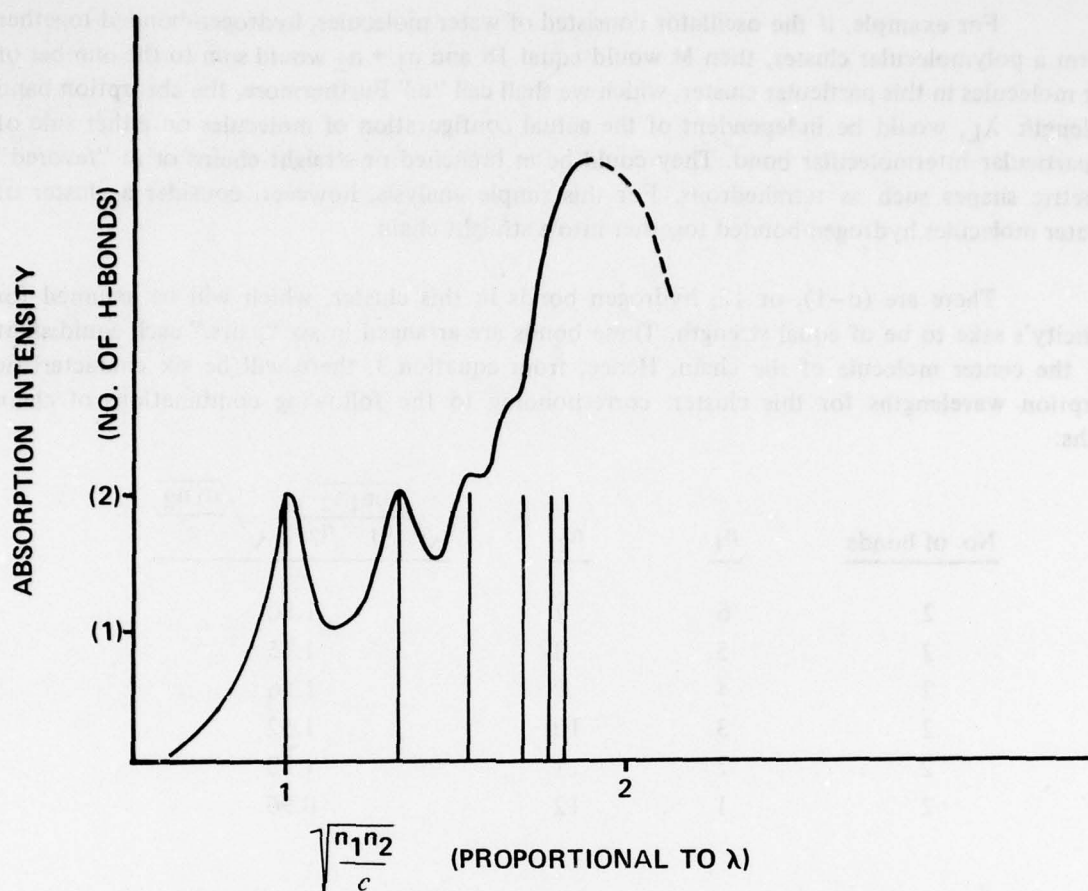


Figure 2. Theoretical Absorption Spectrum for Water Cluster of Size 13 (from Equation 3)

From purely empirical observations, Carlon^{1,2} found such a relationship in the infrared emission spectra of cooling steam clouds. He found an absorption maximum, or λ_{\max} , at $8.66 \mu\text{m}$ which he attributed to polymolecular water clusters of size 13 (i.e., $c = 13$). In such observations, the statistical distributions of cluster sizes must be considered in addition to vibrational symmetries. Nevertheless, Carlon's data provide interesting results when used to evaluate K in equation 3, where

$$\lambda_L = 4.8 \sqrt{\frac{n_1 n_2}{n_1 + n_2}} \quad (4)$$

and, for the "special case,"

$$\lambda_{\max} = 2.4 \sqrt{c} \quad (5)$$

From the observations^{*,3-5} of many workers relating saturation ratio (fractional relative humidity, here designated "s") of water vapor or moist air to mean water cluster size $(c)_{\text{mean}}$, Carlon deduced the simple relationship:

$$(c_1)_{\text{mean}} - (c)_{\text{mean}} = -\ln(s) \quad (6)$$

where, at atmospheric pressure and near-standard conditions, $(c_1)_{\text{mean}}$ is the mean cluster size at saturation ($s = 1.0$) and $(c)_{\text{mean}}$ is the mean cluster size at any value of "s" other than 1.0. Since in cooling steam, $s = 1.0$ to a good approximation, Carlon attributed the observed infrared emission/absorption peak at $\lambda_{\text{max}} = 8.66 \mu\text{m}$ to the cluster size $(c_1)_m = (c)_m = 13$ molecules per cluster. These observations then made it possible to find evidence of wavelength-shifted absorption peaks in long-path infrared water-vapor measurements of Bignell,⁶ Arefev, *et al.*,⁷ and other workers for whose measurements values of (s) were given or could be determined from the reported data. This work strongly suggested that absorption by polymolecular clusters of water in open atmospheres was responsible for infrared "continuum" absorption previously attributed to water "vapor" alone. The good agreement found by Carlon between equations 4, 5, and 6 and infrared spectral measurements further suggests that, since equations 4 and 5 were developed for simple two-body oscillators without regard for more complex vibrational modes, these simple modes may be the only spectrally active ones in the infrared at least to a 13- μm wavelength — that is, more complex modes may give rise to water cluster absorptions at much longer infrared wavelengths in a manner analogous to that in which complex modes of interatomic H—O vibrations produce vapor absorption bands at wavelengths much greater than 2.66 μm , where simple stretching is the mechanism.

IV. IONIC NUCLEATION OF WATER CLUSTERS.

C.T.R. Wilson,^{8,9} whose work was beautifully summarized by J. G. Wilson,¹⁰ showed that in a cloud chamber different kinds of "foreign" nuclei could be successively removed by pressure or volume cycling until, at some point, a supersaturation of $s = 4.2$ was found necessary to form droplets in damp air. Wilson showed that this was the condition for droplet formation on small ions which served as nuclei for individual water molecules. He found the critical cluster size for water to be about $c = 30$; that is, a cluster of 30 molecules could spontaneously form a tiny droplet. But, since a cluster of size 30 could not be attained without supersaturation and Wilson's observations depended upon light scattering from droplets formed within his chamber, the fate of smaller clusters always present in moist air at atmospheric pressure apparently escaped notice. Equation 6 has been used to show that $(c)_{\text{mean}} =$ approximately 13 when $s = 1.0$. In figure 3, equation 6 can be used to represent the vertical portion of the equilibrium curve labeled "ion" in the region $(s) \leq 1.0$.

*Harden, C. S., Chemical Systems Laboratory, Aberdeen Proving Ground, Maryland. Private discussions on charged water cluster size distributions as functions of saturation ratio based upon quadrupole mass spectrophotometric measurements. July 1976.

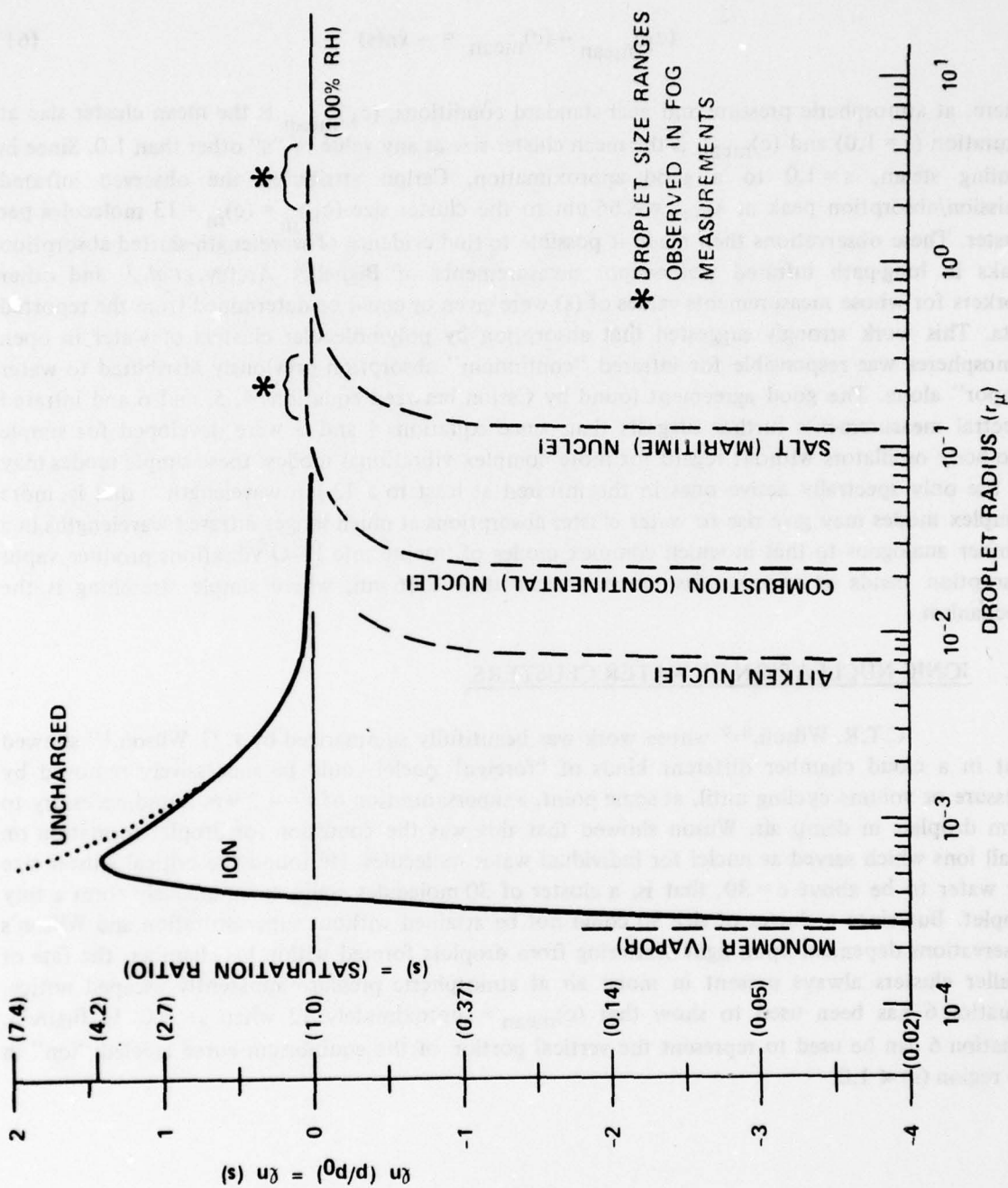


Figure 3. Equilibrium Curves for Water Clusters and Droplets

Under some environmental conditions, the mass fraction of water vapor present as water ion clusters can be of the same order of magnitude as the fraction of liquid water formed as droplets on comparatively much larger "foreign" nuclei. In near-fog conditions, the cluster concentration can be very large. Browne* has shown that vapor-saturated air used to pressurize an adiabatic expansion cloud chamber can yield the majority of its vapor mass as liquid droplets upon rapid chamber decompression – that is, extensive clustering on ions must occur so that, given a supersaturation of $s = 4.2$, most water vapor can be converted to liquid droplets rather than 1% to 2% of all vapor as in heavy natural fogs. Browne used an electric arc for ion enrichment of the moist airstream, but similar yields apparently could be obtained without the arc.

In figure 3, the radii of water clusters over the normal range of atmospheric moisture content, $0.10 \leq (s) \leq 1.0$, are fairly constant. These radii correspond to mean cluster sizes of between 11 and 13, from equation 6. The radii of droplets formed on foreign nuclei are much more sensitive to changes in (s) , especially at higher values of (s) . Thus, under higher-humidity conditions, the optical scattering of rapidly-growing droplets formed on foreign nuclei is often found to dominate the absorption of water clusters in the infrared. But, as the wavelength of observation in the infrared increases, the role of the clusters in determining overall extinction is found to be increasingly important.

From the work of Wilson and many others, one may infer that a water cluster of about 30 molecules is that size where the inter-attractive forces between water molecules become sufficiently well organized to hold together the smallest possible droplet. Although ionic nuclei may be necessary to assist the process of growth (much as foreign nuclei assist droplet growth to comparatively much larger sizes), a cluster of size 30 or more becomes a droplet due to hydrogen-bonding, intermolecular forces which give droplets larger than this measurable properties such as surface tension. Thus, at about size 30, the transitional region is found between water clusters and liquid water. Liquid water is found to be nearly completely hydrogen-bonded or clustered (which is really the same thing for our purposes). The liquid contains clusters of mean size larger than 30, as will be shown presently. The vapor, at least at atmospheric pressure, cannot contain clusters of mean size much larger than about 13. If the saturation of a vapor sample in a cloud chamber were increased, the mean cluster size would increase also from 13 at $s = 1$ to larger values. At $s = 4.2$ (figure 3), some larger clusters on the upper "tail" of the cluster size distribution would, in fact, become liquid droplets. In effect, they would cross the peak of the "ion" curve in figure 3, "sliding down the hill" to become large, stable liquid water droplets by combining with countless other super-critical clusters or, perhaps, just by gathering additional water from surrounding vapor which they would serve to nucleate.

*Browne, P. F., University of Manchester Institute of Science and Technology, Manchester, England. Private discussions of data obtained in work sponsored by U.S. Army Research and Standardization Office (Europe), 1976; corona discharge as an ion source for cloud chamber nucleation suggested to P. F. Browne by J. Latham also of the University of Manchester Institute of Science and Technology.

V. LIQUID WATER.

The most common estimate of mean cluster size in liquid water, $(c)_{\text{mean}}$, seems to be about 39. Though the existence of much larger clusters in the liquid phase has been reported, numbers ranging from 39 to about 46 seem most consistent with recent work. If the nature of hydrogen bonding in the liquid phase is substantially the same as it is in clustering subcritical masses of molecules in the vapor phase, then one would expect from equation 5 that, for $(c) = 39$, $\lambda_{\text{max}} = 15.0 \mu\text{m}$, approximately. This result agrees well with the observation of an absorption peak or transmission minimum at $15 \mu\text{m}$ in the spectrum of a liquid water film shown in figure 4.

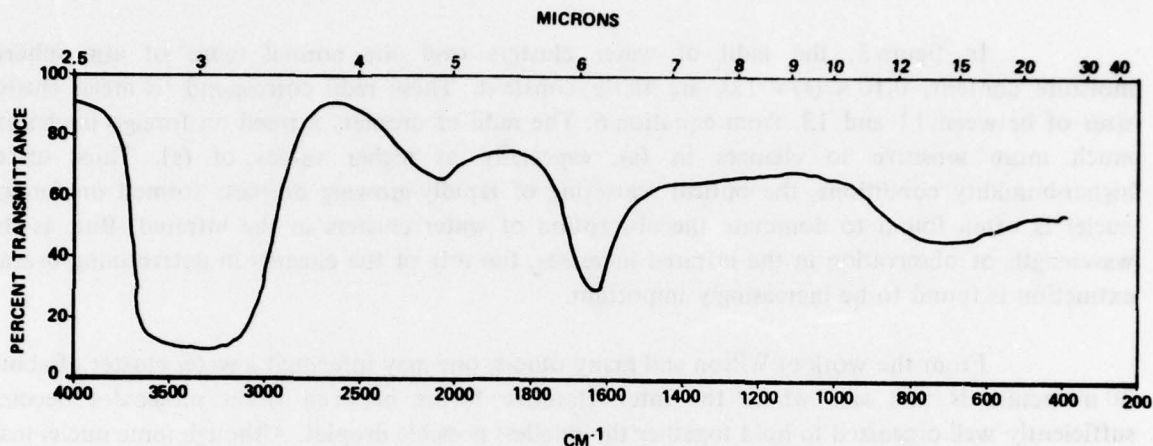


Figure 4. Infrared Transmittance of Liquid Water

Since the constants of equations 4 and 5 were evaluated by Carlon from steam observations, with both liquid and water vapor phases present, such agreement is perhaps not surprising. The liquid spectrum contains "bumps" at other wavelengths besides $15 \mu\text{m}$, which also are not noticed in the spectrum of water vapor. In figure 4, a pronounced feature can be seen near $4.7 \mu\text{m}$, and a broad shoulder can be observed between about 7 and $9 \mu\text{m}$.

Water chemists and spectroscopists have for many years studied infrared spectra of liquid water solutions, investigating wavelength shifts of spectral features with concentrations of dissolved ions in the liquid phase and between the liquid and vapor phases. They have found that the primary bands of water (interatomic) absorption are hardly shifted in wavelength between the vapor and liquid phases.¹¹

<u>Band designation</u>	<u>$\lambda_{\mu\text{m}}$, in vapor</u>	<u>$\lambda_{\mu\text{m}}$, in liquid</u>
ν_1	2.76	2.90
ν_2	6.27	6.10
ν_3	2.66	2.77

The table shows that the great change in phase density between water vapor and the liquid seems to have little effect upon the wavelengths of the absorption bands corresponding to the interatomic vibrations of the water molecule. Thus, the intermolecular bonds of water clusters might be expected to be little affected by phase densities as well. The major differences between spectra of water vapor (figure 1) and the liquid (figure 4) therefore would not be associated with the interatomic bonds within a molecule but with the absorptions attributed to clusters or lattices of water molecules due to hydrogen bonding. The latter have become known as "librational modes," the primary band of which we have already identified at the 15- μ m wavelength in figure 4. Smaller librational bands, at 4.7 μ m, 6.3 μ m, and other wavelengths, are attributed by some researchers "favored" cluster sizes^{1,12} such as (c) = 1 (hydronium ion), (c) = 2 (the dimer), (c) = 4, 5, 7, 11, 13, and so forth. These are considered by some to be the "building blocks" of still larger clusters. But they can, themselves, form chains or branches within larger clusters while contributing their own absorption wavelengths to those of the near-symmetrical wavelengths in the spectrum of the "parent" cluster.

In figure 4 and from equation 4, it can be seen that, according to the foregoing discussion, absorption peaks at 4.7 μ m and in the shoulder at 6.3 μ m could be explained as near-symmetrical vibrational activity by subclusters of sizes 4 and 7, respectively, which in turn could be building blocks of clusters of size about 39, whose near-symmetrical vibrational wavelengths would be near 15 μ m.

The complex refractive index of liquid water, written $(n - ik)$ where $i = \sqrt{-1}$, consists of the density-related "real" index, n , and the "imaginary" index, k . When calculations are performed using the Mie theory and measured complex refractive indices for water, it is found that liquid droplets with radii much smaller than the illumination wavelength are almost pure absorbers. Thus, water clusters, although not actually true "liquid" water when (c) is less than about 30, certainly qualify as pure absorbers at infrared wavelengths. The absorption coefficient, k_L , is related to the imaginary index of refraction, k , by the expression: $k_L = 4\pi k/\lambda$; that is, the imaginary index of liquid water is a wavelength-corrected form of the absorption coefficient. It follows that the spectrum of the imaginary index of liquid water is the spectrum of the interatomic and intermolecular bonds comprising bulk liquid water and that, in the spectral regions between interatomic absorption peaks (i.e., in "windows"), it is nearly the spectrum of water cluster absorption where (c) = 39, approximately.

The absorption coefficient spectrum calculated for liquid water from the data of Hale and Querry¹³ is shown in figure 5. The interatomic bands near 2.8 μ m and 6.1 μ m stand out clearly. The remaining spectral features (with the possible exception of the small peak near 50 μ m) are attributed to intermolecular or cluster absorption. Among the latter are the "librational" peaks at 4.7 μ m and 15.0 μ m. Since the peak intensity of the absorption band at $\lambda_{\text{max}} = 15.0$ μ m should be proportional to the number of hydrogen bonds per cluster per gram of liquid water, for a straight chain this would be due to 38 bonds per cluster per gram of sample. Since, at the peak, $k_L = 0.337 \mu\text{m}^{-1}$ at $\lambda_{\text{max}} = 15 \mu\text{m}$, the average absorption per hydrogen bond is proportional to $0.337/38$, or approximately $0.009 \mu\text{m}^{-1}$ per gram of sample. If so, then the peak in figure 5 at 4.7- μ m wavelength attributed to clusters of size (c) = 4, each having three hydrogen bonds, should have a maximum value of k_L of about $0.027 \mu\text{m}^{-1}$. The observed value is 0.04, which may include

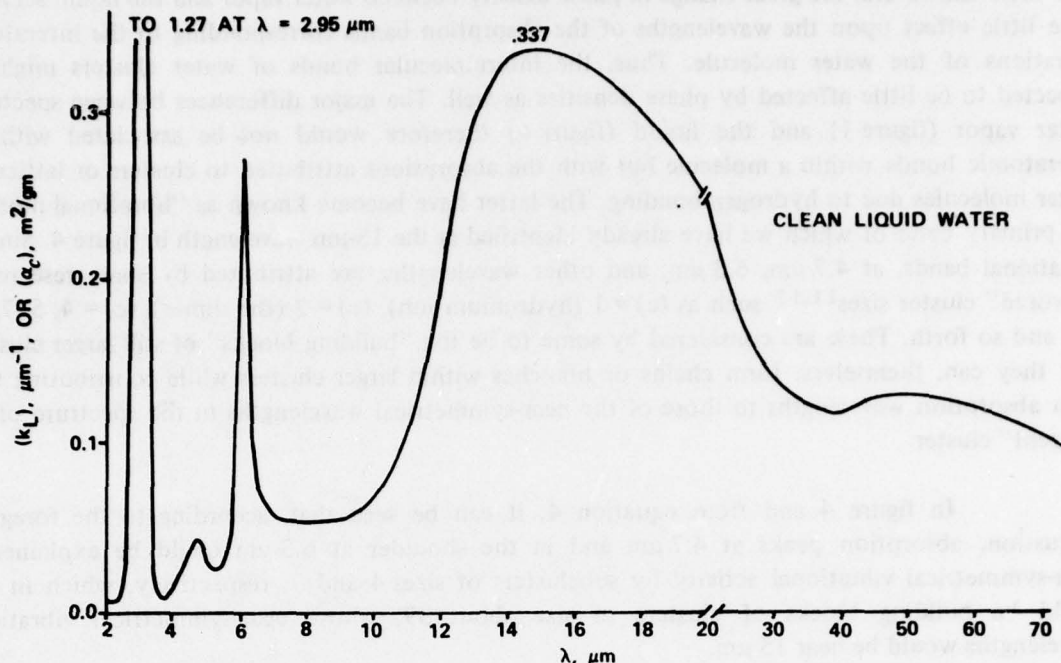


Figure 5. Absorption Coefficient Spectrum for Liquid Water

some contribution from the shoulders of the interatomic absorption bands at $2.8 \mu\text{m}$ and $6.1 \mu\text{m}$. If we assume that the absorption coefficient in any "window" region between interatomic absorption bands is due entirely to water clusters, then a very useful alternative expression can be written for the absorption coefficient of intermolecular hydrogen bonds which is normalized to the average bond absorption per molecule of water in the sample.

The number of molecules per gram of liquid water is $6.02 \times 10^{23}/18 = 0.334 \times 10^{23}$. If $(n_c)_\ell$ is the fraction of these molecules actually clustered or hydrogen bound, then the number of bound molecules per gram of liquid water is $0.334 \times 10^{23} (n_c)_\ell$. These molecules, at λ_{max} , will have an absorption coefficient of $0.337 \mu\text{m}^{-1}$ or $0.337 \text{ m}^2/\text{gm}$, and the absorption coefficient per molecule of water will be $0.337/0.334 \times 10^{23} (n_c)_\ell$ or approximately $10^{-23}/(n_c)_\ell \text{ m}^2$ per bound molecule at λ_{max} , which is the same as $10^{-19}/(n_c)_\ell \text{ cm}^2$ per bound molecule. If the bound molecules are now dispersed in water vapor as clusters, where they represent a fraction $(n_c)_v$ of all water molecules present, their absorption coefficient will be approximately $10^{-19} (n_c)_v/(n_c)_\ell \text{ cm}^2$ per molecule of water vapor. By including a correction for total water vapor concentration, this result can be used to write:

$$(C_s^0)_\lambda_{\text{max}} = \frac{7.6 \times 10^{-17} (n_c)_v}{(s) (p_o)_\theta (n_c)_\ell} \quad (7)$$

where $(C_s^0)_\lambda$ is a popular "self-broadening" absorption coefficient for water "vapor," having the units $\text{cm}^2/\text{molecule vapor/atmosphere vapor}$. We shall return to equation 7 in subsequent discussion.

There is very strong evidence to suggest that the value of $(n_c)_q$ in equation 7 is near 1.0 at standard conditions since nearly complete hydrogen bonding or clustering occurs there. Recalling Wilson's finding that, under these standard conditions, water molecules in cluster sizes greater than about $(c) = 30$ become incipient, hydrogen-bonded liquid droplets, the liquid state can be considered as an assemblage of clusters of mean size near 39, made up of "favored" subclusters of sizes like 4, 5, 7, and 13. And if liquid water is made up mostly of clusters then the density of water clusters, ρ_c , must be about 1.0 gm/cc as well. Therefore, equation 7 should produce approximately correct results with experimental data if $(n_c)_q$ is taken as 1.0 and if other assumptions are valid including the assumption that hydrogen bonds in liquid water have approximately the same molecular absorption coefficient as hydrogen bonds in water clusters formed in the vapor phase.

One of the major pieces of evidence that water in the "pure" liquid state is completely clustered is the fact that the introduction of ions into the liquid in considerable concentrations invariably results in reduced infrared absorption attributable to clusters. Many workers¹⁴⁻¹⁶ have studied effects of ions in liquid water and in ice. The work of Querry, *et al.*,* with $ZnCl_2$ solutions is both recent and helpful to the present discussion. Some of Querry's* data are plotted as absorption coefficients in figure 6.

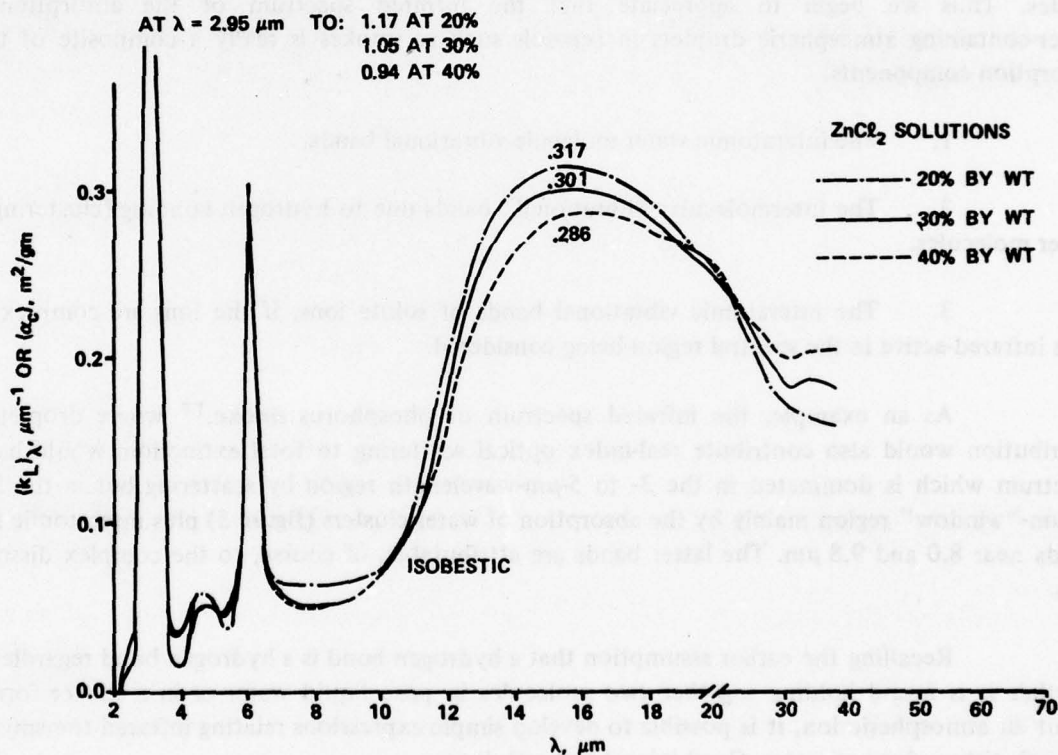


Figure 6. Absorption Coefficient Spectra for $ZnCl_2$ Solutions in Liquid Water

* Querry, M. R., University of Missouri, Kansas City, Missouri. Private discussions of refractive index measurements of water solutions of $ZnCl_2$; data obtained under contract to U.S. Army Research Office.

As the mass fraction of ZnCl_2 in solution is increased, there is some slight evidence of a shift in λ_{max} toward longer wavelengths. This would indicate that, even in liquid water solution, the Zn^{++} and Cl^- ions (themselves not infrared-active in this wavelength region) were helping to nucleate water clusters of somewhat longer chain length. From equation 5, the increase in mean cluster size is of the order from 39 to 46. But the value of the absorption coefficient is seen in figure 6 to steadily *decrease* from the peak value of $0.337 \mu\text{m}^{-1}$ (figure 5) in a manner proportional to the amount of salt added, with solution density corrections made. The salt, in displacing water and its hydrogen bonds from solution, serves to "dilute" the absorption coefficient. From equation 7, it has the effect of changing $(n_c)_\phi$, as well as, possibly, ρ_c . The direction of change in value of $(n_c)_\phi$ obviously is toward smaller mass fraction. If this mass fraction had not been near 1.0 in "pure" water to begin with, it is likely that added ions would have stimulated cluster formation and increased, rather than decreased, the absorption coefficient. It is possible that the displacement of λ_{max} toward longer wavelengths from its "pure" water value of $15.0 \mu\text{m}$ is related to the value of $(n_c)_\phi$ before the salt was added to that after the salt was added.

If a complex salt such as a phosphate or sulfate is added to liquid water, the ions themselves contribute to the infrared spectrum below $13 \mu\text{m}$ because of *their* interatomic vibration modes. Thus we begin to appreciate that the infrared spectrum of the absorption by water-containing atmospheric droplets in aerosols such as smokes is really a composite of three absorption components:

1. The interatomic water molecule vibrational bands.
2. The intermolecular "librational" bands due to hydrogen bonding (clustering) of water molecules.
3. The interatomic vibrational bands of solute ions, if the ions are complex and thus infrared-active in the spectral region being considered.

As an example, the infrared spectrum of phosphorus smoke,¹⁷ where droplet-size distribution would also contribute real-index optical scattering to total extinction, would have a spectrum which is dominated in the 3- to $5\text{-}\mu\text{m}$ -wavelength region by scattering but in the 8- to $13\text{-}\mu\text{m}$ -*"window"* region mainly by the absorption of water clusters (figure 5) plus interatomic P—O bands near 8.0 and $9.8 \mu\text{m}$. The latter bands are attributable, of course, to the complex dissolved ions.

Recalling the earlier assumption that a hydrogen bond is a hydrogen bond regardless of whether it is found holding together two molecules in pure liquid water or in a cluster forming about an atmospheric ion, it is possible to develop simple expressions relating infrared transmission through either phase of water. Combining Lambert's law

$$\ln(1/T_\phi)_\lambda = \alpha_{\phi\lambda} C_\phi L_\phi \quad (8)$$

for the case where "droplet" radii are much smaller than the illumination wavelength with the absorption coefficient expression for hydrogen-bonded water clusters per gram of sample (p 15), we get:

$$\ln(1/T_{\phi})_{\lambda_{\max}} = \frac{0.009(k)(c-1)_{\phi}(n_c)_{\phi}(C)_{\phi}(L)_{\phi}}{\rho_c} \quad (9)$$

where $(n_c)_{\phi}$ and ρ_c are taken near unity in liquid water, $(C)_{\phi} = 10^6 \text{ gm/m}^3$ in the liquid or approximately $289 \cdot (s)(p_o)/\theta_k$ in moist air or in water vapor (p_o = saturation vapor pressure, mmHg, of water at temperature, θ_k , degrees Kelvin), and $(L)_{\phi}$ = path length, meters, through either phase of water. It is instructive to compare the parameters of the vapor and liquid cases for equal transmittances at λ_{\max} ; that is, the right hand side of equation 9 can be written both for water vapor and liquid water, and the resulting expressions can be set equal to each other:

$$\frac{(n_c)_v}{(n_c)_l} = \frac{(c-1)_l C_l L_l}{(c-1)_v C_v L_v} \quad (\text{SPECIAL CASE}) \quad (10)$$

In practice, it is found that $(n_c)_v \ll (n_c)_l$. $(n_c)_v$ is dependent upon parameters such as the number of ions in the vapor sample, the saturation ratio (s) and its effect upon mean cluster size, and other variables not of concern when dealing with the relatively uncomplicated liquid phase. For λ_{\max} , $(c-1)_l$ is taken as 38 and $(c-1)_v$ averages 11 over the range $0.1 \leq (s) \leq 1.0$ found in real atmospheres (equation 6). Substituting known or approximate values into equation 10 yields:

$$(n_c)_v \approx \frac{12,000 (\theta_k) L_l}{(s)(p_o) L_v} \quad (\text{SPECIAL CASE}) \quad (11)$$

where L_l is the path length through "pure" liquid water at λ_{\max} (15.0 μm) required to give the same infrared transmittance as a path length L_v of water vapor at its $\lambda_{\max} = 2.4\sqrt{c}$ (equation 5), where (c) can be obtained from equation 6. Referring to spectra for liquid water such as figure 5, it is found that, at $\lambda_{\max} = 15.0 \mu\text{m}$, a liquid film only 2.06- μm thick will absorb 50% of incident radiation. If we take transmittance $T_{\phi\lambda}$ for the special case of equations 10 and 11 as being equal to 0.5, L_l as $2.06 \times 10^{-6} \text{ m}$, and other parameters as discussed, it is found that, for an equivalent 0.5 transmittance by water vapor at its λ_{\max} , the required path length is 9124 meters. The ratio L_l/L_v is 2.6×10^{-10} and, for 0.5 transmittance,

$$(n_c)_v \approx 2.7 \times 10^{-6} \frac{(\theta)_k}{(s)(p_o)} \quad (\text{SPECIAL CASE, } T_{\phi\lambda_{\max}} = 0.5) \quad (12)$$

The relationships between path lengths and other parameters required for equal cluster absorption at λ_{\max} in the vapor and liquid phases are shown in figure 7. The vapor duct (left in figure 7) and the liquid film (right) both will have transmittances, at their λ_{\max} wavelengths, of 0.5. Using equation 9, it can be calculated that, in real atmospheres, the numbers of ions which would be necessary to serve as nuclei for water clusters having observed infrared absorption are on the order of 10^{15} per liter. These values are much higher than those commonly quoted for other mobile ion concentrations in the atmosphere.

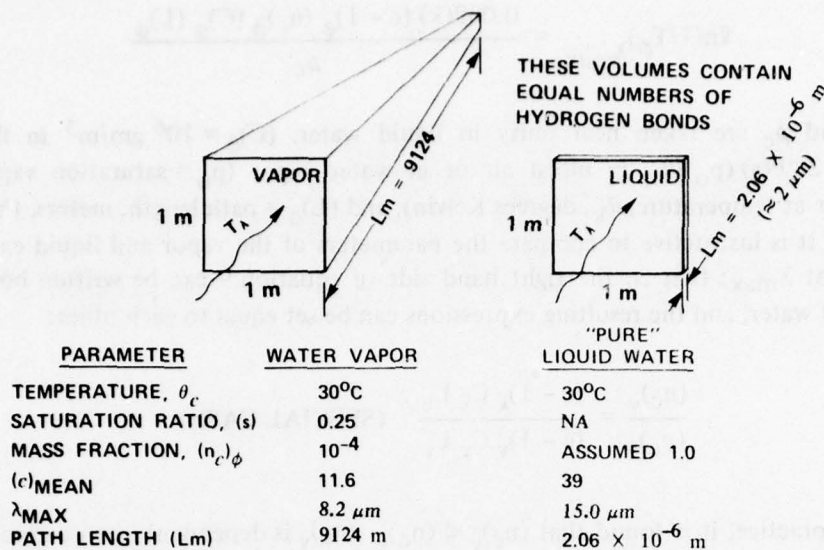


Figure 7. Comparison of Vapor (left) and Liquid (right) Water Samples for Equal Absorption at λ_{max}

VI. APPLICATIONS OF WATER CLUSTER THEORY.

In real atmospheres, over the normal range of atmospheric pressure and saturation ratios $0.1 \leq (s) \leq 1.0$, one application of water cluster theory is in the consideration of the phenomenon known as *infrared water continuum absorption*. In long-path spectral measurements of water vapor or moist air, anomalous absorption is often found which cannot be related to water vapor or droplet concentrations known to be present. This water "continuum" absorption has a spectrum similar to that shown in figure 2; that is, the absorption increases with wavelength and in the 8- to 13- μm -window region it is 10 to 20 times as intense as it is near the 4- μm wavelength. In addition, there are many data taken for the 8- to 9- μm -wavelength region which have been considered erroneous because they were unusually large. A complication of such infrared transmission measurements (from which absorption data are derived) is that they are often taken at a single wavelength. For example, the CO_2 laser wavelength of 10.6 μm is very popular for atmospheric or long-path optical cell measurements. From our discussion of water cluster infrared absorption, it is clear that the λ shift (equation 5) is an immediate source of confusion in single-wavelength measurements.

Since the position of λ_{max} in the vapor phase depends upon mean cluster size (equation 5) and thus upon saturation ratio (s) (equation 6), it is apparent that anything which changes "s" will also shift λ_{max} . Such shifts can, therefore, arise from a simple change in temperature at a constant water sample concentration in water vapor or in moist air.

Although equations 7 and 9 give very good agreement between theory and observation under standard conditions and when λ_{max} is the wavelength at which transmittances

actually are measured, it is found that agreement cannot be obtained under two conditions: (1) when a fixed observation wavelength is used and (2) when the temperature deviates significantly from usual ambient conditions. The cause of (1) is the λ shift which we have already considered, using equations 5 and 6. The cause of (2) is the temperature dependency of $(n_c)_v$ upon (s) ; that is, while $(n_c)_v$ is linearly dependent upon (s) , the constant of proportionality is found to increase with temperature. This causes $(C_s^0)_\lambda$ (equation 7) to be quite independent of (s) and at the same time makes it temperature-dependent in a complex way involving (p_0) . It also causes an apparent pressure-squared dependency of the vapor absorption coefficient (equation 9) which is, in reality, a pressure-squared dependency of the concentration of water clusters present in a given sample. These two conditions, (1) and (2), will now be discussed in greater detail.

Consider the solid curve in figure 8, which is the spectrum in steam at $(s) = 1.0$ attributed by Carlon to water clusters. λ_{\max} is $8.66 \mu\text{m}$, for which, from equation 5, $(c)_{\text{mean}} = 13$. For comparison, the dashed curve of figure 8 represents $(s) = 0.1$, where $(c)_{\text{mean}} = 10.7$ and $\lambda_{\max} = 7.85 \mu\text{m}$. At the $10.6\text{-}\mu\text{m}$ laser wavelength, the absorption measured when $(s) = 1.0$ (point "A") will have fallen to point "B" if (s) is caused to fall to 0.1, perhaps in response to a temperature increase. This change in relative absorption will have occurred mainly because of the λ shift and only secondarily because of the somewhat smaller cluster absorption coefficient at the lower saturation ratio. Errors of this type can be corrected for by knowing the cluster absorption spectra and the amount of wavelength shift. Errors of more than a factor of two, due to λ shift alone, would be quite uncommon.

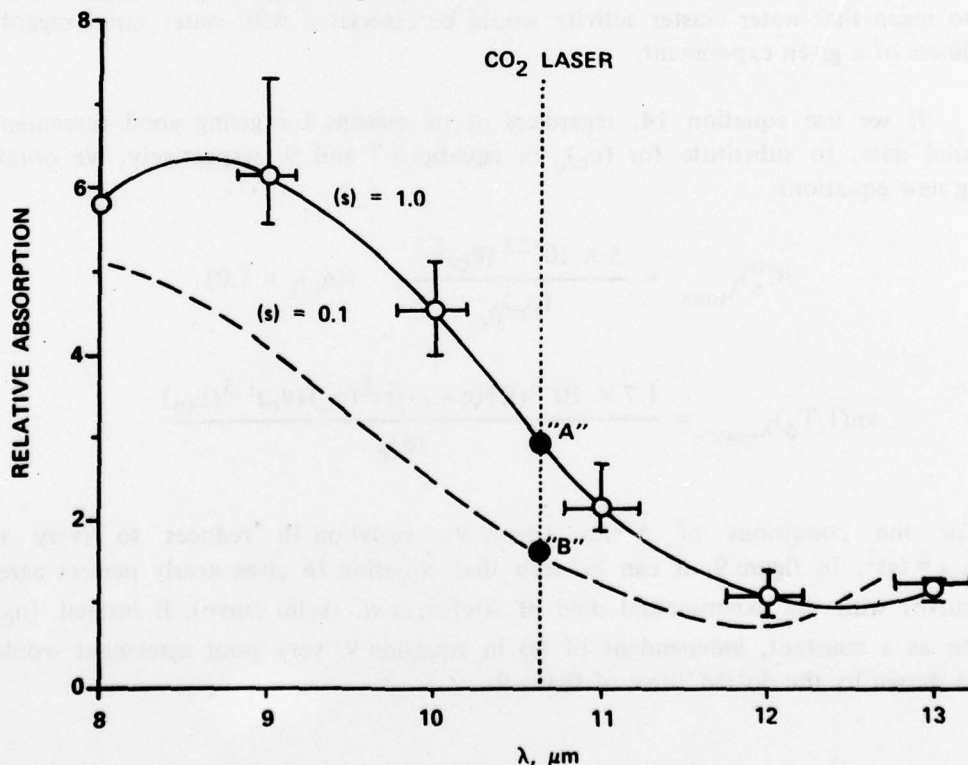


Figure 8. Changes in Water Vapor Absorption with Changes in Saturation Ratio

The dependency of $(n_c)_v$ upon (s) and upon temperature (θ) is of fundamental importance to the understanding of water cluster behavior and the atmospheric infrared absorption of clusters. From careful calculations using equation 7 and infrared absorption data obtained by many workers, it has been determined that the dependence of $(n_c)_v$ upon (s) can be expressed in the form:

$$(n_c)_v = (K_\theta) (s) \quad (13)$$

where (K_θ) is equal to 6×10^{-5} at $\theta_c = 20^\circ$, 46×10^{-5} at $\theta_c = 85^\circ$, and 92×10^{-5} at $\theta_c = 115^\circ$, for example. Purely as a convenience in calculation, it is found that a good approximation to the temperature dependency of (K_θ) is a term proportional to $(\theta_c)^{1.5}$:

$$(n_c)_v \approx 6.6 \times 10^{-7} (\theta_c)^{1.5} (s) \quad (14)$$

The appearance of a 1.5 power of temperature in any expression involving cluster fractions or concentrations in water vapor is interesting because it is known that the dissociative ion product of water also has a $(\theta_c)^{1.5}$ dependency. In other words, the appearance of this term in an empirical equation such as equation 7 at least admits the possibility that the ions necessary for cluster nucleation at higher temperatures could come from the dissociation of water itself. If so, cluster concentrations at higher water vapor temperatures might be explained in terms of "self"-nucleation by dissociative ions of water itself without the need for "foreign" ions. This would also mean that water cluster activity would be associated with water vapor regardless of the cleanliness of a given experiment.

If we use equation 14, regardless of its reasons for giving good agreement with experimental data, to substitute for $(n_c)_v$ in equations 7 and 9, respectively, we obtain two interesting new equations:

$$(C_s^0)_{\lambda_{\max}} = \frac{5 \times 10^{-23} (\theta_c)^{1.5}}{(p_o)_{\theta_c}} \quad ((n_c)_\ell = 1.0) \quad (15)$$

and

$$\ln(1/T_\phi)_{\lambda_{\max}} = \frac{1.7 \times 10^{-6} (K) (c-1) (s)^2 (p_o) (\theta_c)^{1.5} (L_m)}{(\theta)_k} \quad (16)$$

where, for the conditions of Arefev (figure 9), equation 16 reduces to (very nearly) $\ln(1/T)_{10.4} = (s)^2$. In figure 9, it can be seen that equation 16 gives nearly perfect agreement (dashed curve) with the experimental data of Arefev, *et al.* (solid curve). If instead, $(n_c)_v$ had been taken as a constant, independent of (s) in equation 9, very poor agreement would have resulted as shown by the dotted curve of figure 9.

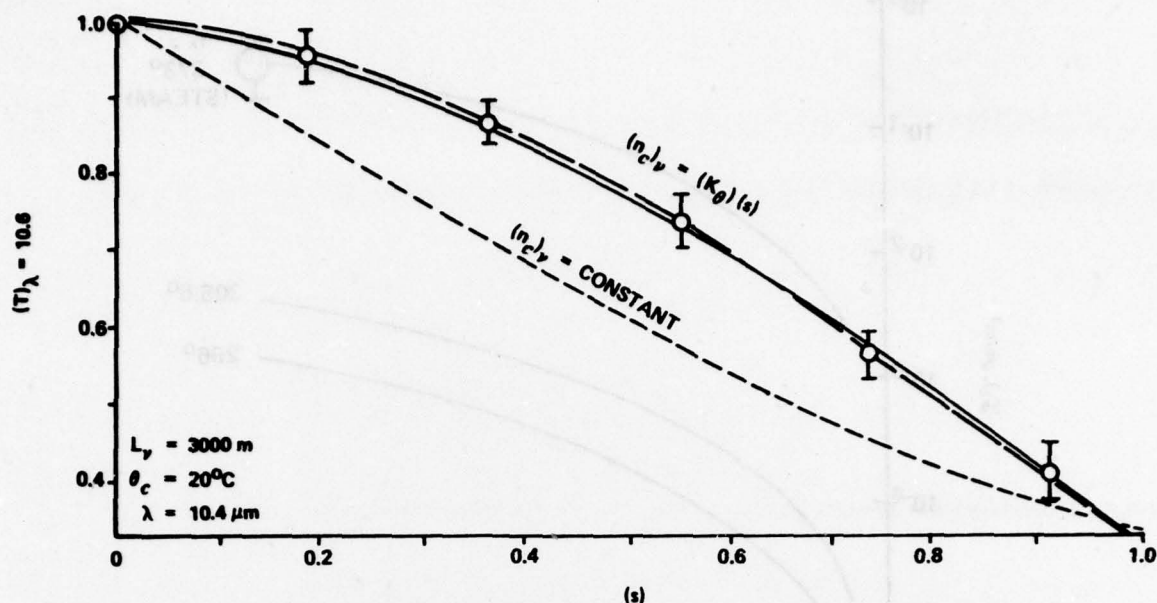


Figure 9. Comparison of the Data of Arefev, *et al.*,⁷ to Water Cluster Theoretical Predictions

From equation 15, $(C_s^0)_\lambda$ is shown as being independent of (s) . In the data of Arefev, *et al.*, and others, this is indeed seen to be the case. However, the temperature-dependent ratio $(\theta_c)^{1.5}/(p_o)_{\theta_c}$ is found to be complex in behavior, decreasing from a value of 5.1 at 20°C to a value of, for example, about 1.32 at 100°C. This gives the predicted value of $(C_s^0)_\lambda$ a negative temperature dependency of several percent per degree.

Since the concentration of water clusters in vapor, C_c (gm/m³), is equal to $(n_c)_v$ times the vapor concentration which is approximately $(289)(s)(p_o)/\theta_k$, it is calculated from equation 14 that:

$$C_c \approx \frac{1.9 \times 10^{-4} (s)^2 (p_o) (\theta_c)^{1.5}}{(\theta)_k}; \quad (17)$$

that is, it is the concentration of water clusters in vapor that has a pressure-squared dependency attributed to the "vapor" absorption coefficient in the infrared. Equation 17 is plotted in figure 10.

As figure 10 shows, water cluster concentrations in saturated steam at 100°C can approach 1 gm/m³, corresponding to cluster mass fractions, $(n_c)_v$, on the order of 0.00066. However, if equilibrium clusters were allowed to form in steam at 100°C and if the steam were then allowed to cool while saturation humidity ($s = 1.0$) were maintained, quite possibly the cluster concentration, once established, would be maintained even as the steam cloud cooled to near-ambient temperatures. These were almost precisely the experimental conditions established by

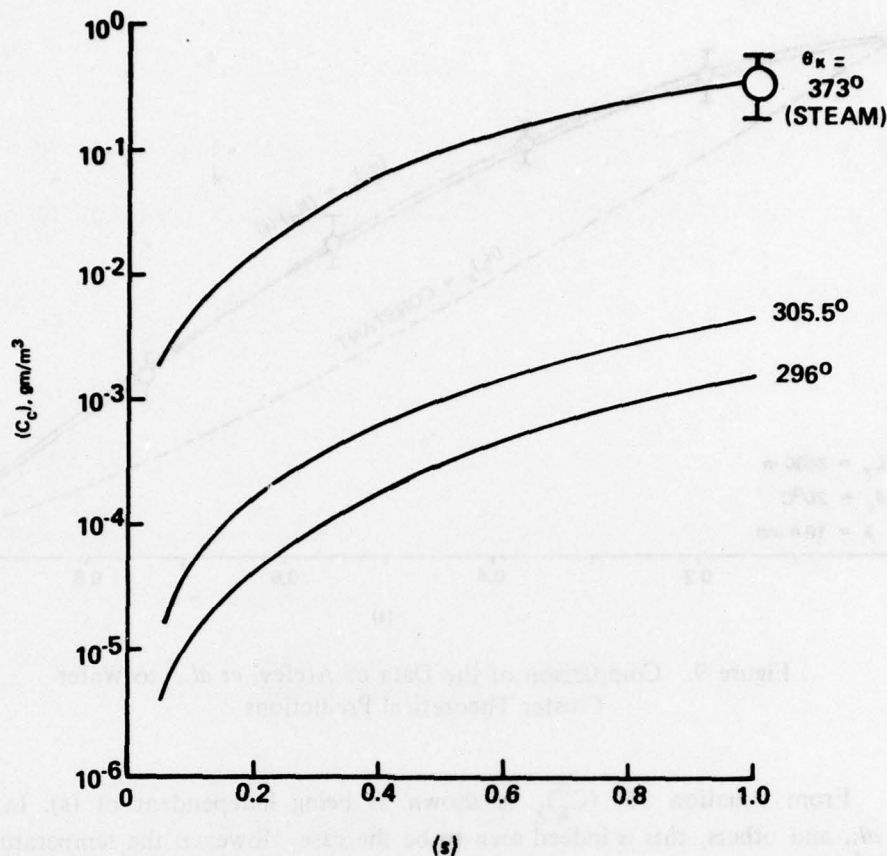


Figure 10. Dependency of Equilibrium Water Cluster Concentration, in Vapor, Upon Saturation Ratio (s) and Temperature (θ)

Carlson,² who computed water cluster concentrations as large as 0.55 gm/m^3 in steam clouds cooled to 32.5°C and who noted a sudden and large reduction in the magnitude of the observed emission/absorption spectrum (solid curve, figure 8) when saturation humidity was lost. Thus Carlson probably produced water cluster concentrations in steam at 100°C , in the range shown by the vertical bar in figure 10, and maintained these concentrations at lower temperatures since the clusters, once nucleated and formed, would not evaporate so long as $s = 1.0$. In a similar manner, water droplets, once formed on soluble nuclei, are not evaporated unless saturation humidity is lost. Thus if Carlson were able to maintain water cluster concentrations on the order of 0.55 gm/m^3 , at temperatures near 32.5°C (where saturated water vapor has a concentration of 34.7 gm/m^3), his cluster fraction would have been $0.55/34.7 = 0.016$ or roughly that of the amount of large liquid droplets present in a heavy fog. In this sense, a fraction of water clusters at 32.5°C much larger than that under normal equilibrium conditions would have existed for Carlson's measurements of the water cluster spectrum. This enhanced cluster concentration would have accounted for the ease with which the spectrum was actually observed by him. Thus, the cluster spectrum (solid curve, figure 8) was observed clearly in a 3-meter optical path where Bignell⁶ and others had found evidence of it over much longer optical paths; i.e., hundreds of meters.

The measurements of Bignell and others also have indicated that the "continuum" absorption spectrum¹⁸ of water vapor, attributed in the present paper to water clusters in the vapor phase, has an absorption maximum near λ_{\max} but that the absorption coefficient continues to increase out to much longer infrared wavelengths. Although the value of $(C_s^0)_{\lambda_{\max}}$ (equation 15) is on the order of 3×10^{-22} near 20°C, measured values of this molecular coefficient are found to increase through at least two additional orders of magnitude as wavelength increases out to at least 40 μm . Thus the λ_{\max} (equation 5) which we have identified in the 8- to 13- μm -“window” region, although probably being the maximum corresponding to simple stretching vibrations of simple clusters (equation 3), does not correspond to the grand maximum value of water cluster absorption at longer wavelengths, where these much larger absorptions apparently are attributable to complex motions of whole water clusters, perhaps rotations. While whole-cluster rotations might be so hindered in the dense liquid water phase so as to produce absorption bands far beyond the infrared region, whole-cluster rotations of the smaller vapor phase clusters in this less dense phase of water might occur near or beyond the 40- μm wavelength. Whatever its origin, the magnitude of the molecular absorption coefficient here attributed to water clusters is on the order of 3×10^{-20} at 36 to 40 μm .

Other applications of water cluster theory suggest themselves. The concept of an infrared cloud chamber is intriguing. While C.T.R. Wilson had to depend upon the formation of light-scattering liquid droplets to determine “end points” in his cloud chamber experiments, operators of long-path infrared cloud chambers could detect water cluster absorptions at sizes well below critical and in sub-saturated rather than super-saturated water vapor or moist air. After cycling to remove “foreign” nuclei, it should be possible to study water clustering and hydrogen bonding on ionic nuclei over long, folded optical paths. Such observations should allow determination of such parameters as cluster size versus saturation ratio on various kinds of ions, locations of λ_{\max} , the precise absorption coefficient spectrum for hydrogen bonds, the uniformity of hydrogen bond strength in clusters of various sizes, and so forth.

Perhaps the most promising application of water cluster theory lies in the exploration of the “connections” that appear to exist between ion-nucleated clusters in the vapor phase and clusters of various “favored” sizes in the liquid phase. Because the vapor phase allows manipulation of parameters which have no counterpart in liquid water, e.g., saturation ratio and cluster concentration, it should be possible to design experiments which will permit the nature of hydrogen bonding or clustering to be better understood. Such observations might disclose a great deal about the nature and “structure” of water-substance in all its physical phases.

VII. RÉSUMÉ.

This report is intended as a handbook for electrooptical applications engineers interested in the effects of polymolecular clusters of water upon the infrared transmission of the atmosphere. It is a compendium of work on the subject ranging from the oldest (C.T.R. Wilson's investigations of ion-nucleated clusters of water performed at the end of the nineteenth century) to the very newest (some of which is not yet generally accepted by the scientific community). The equations and data presented here will enable the infrared engineer to perform calculations of atmospheric transmittance as limited by water clusters, using this as a correction to standard atmospheric transmission models. At the same time, new applications such as the infrared cloud chamber should suggest themselves to the reader.

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WATER CLUSTERS

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